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Mechanisms for the formation of monomers and oligomers
during the pyrolysis of a softwood lignin

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Abstract

The formation of monomers and oligomers during the pyrolysis of softwood lignin has been studied with particular emphasis on the reactivity of coniferyl alcohol (CA), which is the anticipated product of the primary pyrolysis of lignin. Under the pyrolysis conditions ($N_2/250-350^\circ C/5$ min), the lignin contained in Japanese cedar (*Cryptomeria japonica*) as well as the milled wood lignin (MWL) fraction gave the monomeric guaiacols, including CA, coniferyl aldehyde, dihydroconiferyl alcohol, isoeugenol and 4-vinylguaiacol. These products were similar to those obtained from the pyrolysis of CA, although the yields were much lower. The addition of an aprotic solvent, such as diphenoxybenzene (DPB), led to a substantial increase in the recovery of CA from its pyrolysis reaction, likely by inhibiting the formation of the quinone methide intermediates for the polymerization products, whereas the solvent effects were comparatively small for the lignin pyrolysis. Alternatively, the inclusion of a H-donor (1,2,3,10b-tetrahydrofluoranthene) to the DPB led to a substantial increase in the yields of the monomers and oligomers from lignin. Based on the present data, the pyrolytic formation of the monomers and oligomers from the softwood lignin is discussed at the molecular level.

Keywords

Lignin, Pyrolysis, Monomer, Oligomer, Molecular mechanism, Coniferyl alcohol.

1. Introduction

Lignin, which represents about 20-30 wt% of wood, is a potentially renewable resource of aromatic chemicals, because lignin itself is an aromatic polymer composed of phenylpropane-units linked through a variety of different ether (C-O) and condensed (C-C) linkages. Processes for the conversion of lignin to the corresponding monomers are invariably based on heat treatment, such as fast pyrolysis [1]. The pyrolysis of lignin has been studied in the presence of hydrogenation catalysts [2, 3] as well as in the presence of a hydrogen-donor solvent [4, 5] with the aim of improving the yield of the liquefied products.

Given the polymeric nature of lignin, the depolymerization of the lignin chains and subsequent secondary reactions are important steps in the production of low molecular weight (MW) products. During the primary stages of the pyrolysis process, model compound studies [6,7] have indicated that the ether linkages between the phenylpropane-units are cleaved, effectively leading to the breakdown of the lignin polymers, whereas the condensed (C-C) type linkages are comparatively stable and remain largely intact. Model compound studies [6,7] have also suggested that cinnamyl alcohol-type structures such as coniferyl alcohol and sinapyl alcohol represent the primary structures that are formed through the pyrolytic cleavage of the β -ether linkages, which represent the most abundant type of linkage in lignin. The yields of coniferyl alcohol (CA) and sinapyl alcohol from the pyrolysis reactions of lignin and wood,

however, have been reported to be less than those expected from the model compound studies [8-13].

With the aim of identifying the root cause of this discrepancy, we have investigated the reactivity of coniferyl alcohol at temperatures in the range of 200-350°C [14], which covers the temperature range (300-350°C) [15-17] where major weight-losses have been reported to occur from lignin, using thermogravimetric analysis. Coniferyl alcohol tends to condense to form polymerization products rather than undergoing an evaporation process (recovery) or a side-chain conversion reaction, which could lead to the formation of coniferyl aldehyde (an oxidation product), isoeugenol and dihydroconiferyl alcohol (reduction products) or 4-vinylguaiacol bearing a C2 side chain [14]. Thus, differences in the relative efficiencies of the evaporation/condensation/side-chain-conversion processes have been proposed as factors determining the recovery of CA. The high level of condensation reactivity arising from the effective formation of the quinone methide intermediates, which were formed from the conjugated C=C double bond on the CA, has been used as an explanation for the low recovery of CA. Based on these features of the pyrolytic reactivity of CA, it has been suggested that coniferyl alcohol would suffer from the occurrence of secondary reactions such as condensation and side-chain conversion reactions prior to the recovery of CA, even if it was formed from the primary pyrolysis step of the guaiacyl (G)-type lignin.

With this in mind, we describe the pyrolysis behaviors of Japanese cedar wood (*Cryptomeria japonica*) and the milled wood lignin (MWL) fraction. The formation

behaviors of the monomeric guaiacols and oligomers have also been discussed at the molecular level. The roles of aprotic solvent and H-donor in the lignin pyrolysis process have also been discussed.

2. Experimental

2.1 Materials

trans-Coniferyl alcohol (*trans*-CA, **1**) was prepared by the reduction of *trans*-coniferyl aldehyde with sodium borohydride. *cis*-Coniferyl alcohol (*cis*-CA, **2**) was separated from the pyrolysis mixture using preparative thin-layer chromatography (TLC) on a silica gel plate (Kieselgel 60 F₂₅₄, Merck). Dihydroconiferyl alcohol (**4**), isoeugenol (**5**), coniferyl aldehyde (**3**), and 4-vinylguaiacol (**6**) were purchased from Nacalai Tesque Inc. (Kyoto, Japan) as the guaranteed grades and used without further purification. Diphenoxybenzene (DPB) and 1,2,3,10b-tetrahydrofluoranthene were purchased from Tokyo Chemical Co., Ltd. (Tokyo, Japan) as the guaranteed grades and used without further purification. The chemical structures of all of the compounds prepared in this report were confirmed by comparison of their ¹H-NMR spectra with those of the authentic compounds. All of the ¹H-NMR spectra were measured on a Varian AC-400 (400 MHz) spectrometer (Varian, CA, USA). The chemical shifts and coupling constants (*J*) are shown as δ and Hz, respectively.

Japanese cedar wood flour (<80 mesh), which had been pre-extracted with ethanol/benzene (2:1, v/v), and the MWL fraction isolated from cedar wood were used in the current study. The characterization of these samples was described in our previous report [18]. The MWL fraction contained some sugar component (3.0 wt%) from the hemicellulose (hydrolysable sugar content by alditol-acetate method: glucose: 0.6 wt%, xylose: 0.7 wt%, mannose: 0.3 wt%, and arabinose: 0.2 wt%)

2.2 Pyrolysis

An open-top reactor system similar to that used in our previous report [19] was used for the current work. *trans*-CA (5.0 mg) was placed at the bottom of a Pyrex glass tube with an internal diameter of 8.0 mm, length of 300 mm, and wall thickness of 1.0 mm through an evaporation process from a methanol (MeOH) solution. The wood or MWL samples (5.0 mg each) were directly added to the bottom of the reactor. In some experiments, DPB (50 mg) or a mixture of DPB (50 mg) and 1,2,3,10b-tetrahydrofluoranthene (11.4 or 57 mg) was also added to the bottom of the reactor to behave as an aprotic solvent or H-donor, respectively. The air inside the reactor was purged with N₂ using an aspirator connected to the reactor through a three-way tap. The bottom two thirds of the reactor were then placed into a muffle furnace, which had been preheated to a temperature in the range of 250–350°C, through a small hole in the top of the furnace. Following a period of heating for 5 min, the reactor was immediately cooled

120 by flowing air over the reactor for 1 min before being cooled further with cold water for
121 1 min.

122 Following the pyrolysis process, the inside of the reactor was rinsed with MeOH (1.0
123 mL) to recover the MeOH-soluble products and the remaining CA (in the case of the
124 pyrolysis of CA). The MeOH-soluble portions were then subjected to the following
125 analytic procedures.

126

127 *2.3 Product analysis and quantification*

128 The process used for the identification of the products **1-6** has been described in our
129 previous paper [14]. The quantification of these products was mainly conducted by
130 analyzing the MeOH-soluble portions by high-performance liquid chromatography
131 (HPLC) on a Shimadzu LC-10A system (Shimadzu, Kyoto, Japan) using a Cadenza CD
132 C-18 column with a flow rate of 0.7 mL/min at temperature of 40°C. A binary solvent
133 system composed of MeOH and H₂O was used for the HPLC analysis with a gradient of
134 30/70 (0 min) → 45/55 (0 min → 5 min), 45/55 (5 min → 25 min) → 100/0 (25 min →
135 55 min), and 100/0 (55 min → 70 min). The HPLC system was equipped with a UV
136 detector operating at a wavelength of 280 nm. The product yields and recoveries of CA
137 (in the case of the CA pyrolysis) were determined from a comparison of their peak areas
138 with that of 1,2,3-trimethoxybenzene, which was used as an internal standard. For the
139 dihydroconiferyl alcohol, the UV absorption at 280 nm was relatively low, which could
140 potentially lead to a reduction in the accuracy of the quantification provided by the HPLC

analysis. With this in mind, the yield of dihydroconiferyl alcohol was also determined on the basis of the peak area of one of its ^1H -NMR signals (δ 2.65 ppm, t, $J = 7.4$, $\text{C}_\alpha\text{-H}$).

Gel-permeation chromatography (GPC) was used to obtain molecular weight (MW) distribution information for the MeOH-soluble products using the Shimadzu LC-10A system with a Shodex KF-801 column at a flow rate of 0.6 mL/min and a temperature of 40°C. THF was used as an eluent with UV detection at a wavelength of 280 nm.

All pyrolysis experiments were repeated at least twice, and the product yields were not very different in these sets of experiments, although the data presented in this paper were not treated statistically.

2.4 Bond dissociation energy calculation

A density functional theory (DFT) calculation was conducted under AM1 at the B3LYP/6-311+G** level with “Spartan’08” (Wavefunction Inc., CA, USA) to obtain a bond dissociation energy (BDE). A zero-point energy correction was not made in the current study.

3. Results and discussion

The Japanese cedar wood and the MWL fraction were pyrolyzed under N_2 at temperatures in the range of 250-350°C for 5 min, and the resulting pyrolyzates obtained as the MeOH-soluble portions were analyzed by HPLC. The chromatograms (350°C) are

illustrated in Fig. 1 together with a chromatogram from the pyrolysis of CA conducted under similar conditions. From the chromatograms, it was possible to identify *trans*-CA (**1**), *cis*-CA (**2**), coniferyl aldehyde (**3**), dihydroconiferyl alcohol (**4**), isoeugenol (*trans/cis*, **5**) and 4-vinylguaiacol (**6**). In our previous paper, we reported that all of these materials were formed from the pyrolysis of CA [14]. The shapes of the chromatograms were quite similar except for the signals with retention times less than 10 min from the wood sample. These signals may be attributed to the wood polysaccharides, such as cellulose and hemicellulose. The intensities of these signals in the chromatograms from the MWL and the wood samples, however, were much lower than those observed in the chromatogram from CA. These observations suggested that the pyrolysis reactions of the MWL and the wood samples gave the monomeric guaiacols **1-6** in much lower yields than those observed in the pyrolysis of CA. The combined yields of the monomers **1-6** were only 2.1 and 2.7 wt% (lignin-basis) at 350°C for the MWL and wood samples, respectively. Unfortunately, these yields were too low to enable a discussion of the role of CA formation during the pyrolysis of the G-type lignin.

CA is known to polymerize to form polymerization products as opposed to undergoing the evaporation process [14,20,21] or conversion to the side-chain-conversion products mentioned above [14,20]. Conducting the pyrolysis in a solvent would allow for this polymerization reaction to be effectively suppressed. To increase the yields of the monomeric guaiacols from the wood and MWL samples, the pyrolysis was also conducted in diphenoxybenzene (DPB), which is an aprotic solvent. Pyrolysis

conditions including 1,2,3,10b-tetrahydrofluoranthene, which is a H-donor, were also used to develop a better understanding of the influence of the H-donor on the formation of the monomers, because radical mechanisms have been suggested for the side-chain conversions of CA during the pyrolysis. Prior to a discussion of the pyrolysis reactions of the MWL/wood samples, the influences of the solvent and the H-donor on the pyrolysis of CA were also studied. The recoveries of CA, as well as the yields of the monomeric guaiacols **2-6**, from the pyrolysis reactions of CA conducted under neat, solvent and solvent/H-donor conditions are summarized in Fig. 2. The yields of the monomeric guaiacols **1-6** from the pyrolysis of the wood and MWL samples under three different pyrolysis conditions are also summarized in Fig. 3.

For the pyrolysis of CA, the use of the solvent led to an increase in the recovery of CA at all of the temperatures tested in the current study (Fig. 2). The recoveries increased from 14.3 to 40.5% (neat conditions) to 57.6 to 82.0% (in DPB). The values reached 70.8 to 83.7 wt% when the yields of the monomeric guaiacols **2-6** were also included. As illustrated in Fig. 4A, it has been suggested that the quinone methides are important intermediates in the polymerization reactions [14]. The proton-transfer represents an essential step for these reactions because the quinone methide intermediates are formed through heterolysis-type reactions. Under the neat conditions, the intermolecular proton-transfer would only occur in the CA melt. In contrast, however, the occurrence of a proton-transfer step of this type would be ineffective under the solvation conditions in

DPE, as illustrated in Fig. 4A and this would suppress the polymerization reactivity of CA.

The addition of the H-donor to the solution of CA in DPE led to a significant change in the composition of the monomeric guaiacols resulting from the pyrolysis of CA, with the conversion of CA to dihydroconiferyl alcohol (**4**) and isoeugenol (**5**) being enhanced by the presence of the H-donor. This enhancement in the conversion process can be explained in terms of the action of the hydrogen radical, as illustrated in Fig. 4B. The thermal decomposition of 1,2,3,10b-tetrahydrofluoranthene would give rise to the hydrogen radical through the abstraction of the benzyl hydrogen, followed by a β -scission reaction. The resulting hydrogen radical could then add to the C=C double bond of CA to form compounds **4** and **5**, as discussed in our previous paper [14]. Alternatively, these formation mechanisms suggest that the reactions leading to the formation of dihydroconiferyl alcohol (**4**) and isoeugenol (**5**) could be used as probes to provide information about the relative concentration of the hydrogen radical in the pyrolysis environment. This idea will be discussed in greater detail below.

The solvent and the H-donor affected the pyrolysis reactions of the wood and MWL samples in different ways (Fig. 3). The use of the solvent increased the yields of the monomeric guaiacols **1-6** as observed in the pyrolysis of CA, and the H-donor was also very effective for increasing the yields of the monomeric guaiacols. The yields of the monomeric guaiacols **1-6** at a temperature of 350°C increased from 2.1 and 2.7 (neat) → 3.9 and 4.3 (in DPE) → 8.3 and 12.8 wt% (in DPE/H-donor) for the MWL and the wood

samples, respectively. Even the yield of CA tended to increase in the presence of the H-donor, although the recovery of CA during the pyrolysis of CA was reduced significantly as a consequence of side-chain conversion reactions. The discrepancy between the CA and MWL/wood samples can be explained in terms of the characteristic features of the lignin pyrolysis, with model studies reporting that the cleavage of the lignin ether linkages occurs predominantly according to homolytic cleavage mechanisms [22,23]. Accordingly, the pyrolytic cleavage of the lignin ether linkages would release large quantities of radical species, which would tend to form the corresponding radical coupling products even in the aprotic solvent, DPE. It would therefore be necessary to stabilize these radicals through hydrogen donation to provide the monomeric guaiacols. As observed in the pyrolysis of CA, the yields of dihydroconiferyl alcohol (**4**) and isoeugenol (**5**) increased in the presence of the H-donor, likely because of the occurrence of similar mechanisms, as shown in Fig. 4B.

As for the composition of the monomeric guaiacols following the pyrolysis reactions of MWL and wood, at a relatively low pyrolysis temperature of 250°C, the major monomeric guaiacol was found to be coniferyl aldehyde (**3**) [67 (MWL) and 80% (wood), monomer-basis], as opposed to CA [33 (MWL) and 12% (wood), monomer-basis]. Similar results have also been reported by Arias et al. [13] who studied the pyrolysis-GC/MS analysis of pine wood at various temperatures. Increases in the pyrolysis temperature from 250°C to 300 and 350°C led to increases in the amounts of dihydroconiferyl alcohol (**4**), isoeugenol (**5**) and 4-vinylguaiacol (**6**) (Fig. 3).

The preferential formation of coniferyl aldehyde at relatively low temperatures can be understood in terms of the relative amount of radical/H-donor (or H radical), as discussed in Fig. 5. During the primary pyrolysis of the lignin, the pyrolysis environment is considered to be under radical conditions because of the formation of large quantities of radicals through the homolytic cleavage of the lignin ether linkages. Under such H-donor-deficient conditions, these radical species would tend to form the corresponding radical coupling products or be stabilized by abstracting hydrogens from other molecules. The C_γ-hydrogen of CA, which is at the conjugated allyl position, may act as a H-donor to these radicals, and this could result in the formation of coniferyl aldehyde via the release of a hydrogen radical. The resulting hydrogen radical could in turn be used for the stabilization of the radical species, rather than undergoing addition to the side-chain C=C double bonds.

At a higher pyrolysis temperature of 350°C, the pyrolysis environment would change to become richer in H-donor species (H radical). Asmadi et al. [24] have suggested that the hydrogen radicals formed during charring reactions effectively promoted the pyrolytic radical chain reactions of guaiacol and syringol, which were used as model aromatic nuclei of lignin. The charring reaction itself represents a form of polyaromatization. It is generally believed that this process releases hydrogen radicals via similar H-abstraction/β-scission reactions to those discussed for the thermal decomposition of 1,2,3,10b-tetrahydrofluoranthene in Fig. 4B. The presence of enhanced levels of H-donor (H-radical) species would provide an effective explanation of the

increasing yields of dihydroconiferyl alcohol (**4**) and isoeugenol (**5**) observed at the higher pyrolysis temperatures.

A comparison of the results for CA with those from MWL/wood revealed that the MWL/wood tended to produce more 4-vinylguaiacol (**6**) (Figs. 2 and 3). This may be attributed to the elimination of C_γ occurring before cleavage of the β-ether linkages [6]. The resulting vinyl ether structure would form 4-vinylguaiacol.

The lower yields of CA from the pyrolysis reactions of the MWL and wood samples than those expected from the pyrolysis of CA and the model compound study would be attributed to the “polymer effect”. The cleavage of the ether linkages at the terminal groups of the lignin macromolecule would lead to the direct formation of monomer units. This would represent a case very similar to those of the pyrolysis reactions of CA and other model compounds. In contrast, the cleavage of the ether linkages within the polymer would not lead to the immediate formation of monomer units from lignin because of its polymeric nature, and would instead give rise to truncated polymeric units. In these circumstances, the pyrolyzates would remain in the heating zone and undergo secondary pyrolysis reactions, such as radical coupling and side-chain conversion reactions, prior to the formation of monomer units through the cleavage of their ether linkages, because the initial ether cleavage reactions would produce more labile structures containing C=C side-chains and radicals. These “polymer effects” would lead to a reduction in the yield of the monomer and an increase in the concentration of the side-chain conversion products, including compounds **2-6**.

On the basis of a report suggesting that the condensed (C-C) linkages in the lignin macromolecule, which comprise 30-40% of the linkages between the phenylpropane-units in lignin, are stable during the primary pyrolysis of lignin [6,7], we believe that these linkages would remain intact during pyrolysis under the present conditions. This would therefore suggest that the primary pyrolysis of lignin leads to the formation of oligomeric products together with the monomers. The yields of the monomer and oligomer units were estimated on the basis of a schematic softwood lignin structure from the literature composed of 16 phenylpropane-units [25]. The estimated yields were determined under the assumption that all of the ether linkages are cleaved and any further secondary reactions do not occur during pyrolysis (Fig. 6). The estimated yields were found to be 31 (monomer) and 69% (oligomer). These results therefore suggested that the oligomeric products must be produced in much higher yields than the monomeric products. These features also provided an explanation for the comparatively low yields of the monomers from MWL/wood.

Fig. 7 shows the chromatograms obtained from the GPC analyses of the MeOH-soluble portions from the pyrolysis reactions of the MWL and the wood samples. Although the signals observed in the higher MW region (i.e., shorter retention times) than that of CA were very small under the neat conditions, these signals increased significantly when the pyrolysis process was conducted in DPE, and increased even more so when the process was conducted in the presence of the H-donor. These results indicated that the primary oligomeric products with lower volatilities could polymerize to

form insoluble products rather than evaporate, as they would under the neat conditions. This polymerization reaction was effectively suppressed in DPF and in the presence of the H-donor, for reasons similar to those described for the formation of the monomeric products.

All of the results observed in the current paper can be adequately explained by the formation of CA and the subsequent secondary reactions of the CA radical as a major pathway for the pyrolysis of the G-type lignin. The stabilization of the primary radical products with a H-donor in an aprotic solvent was also identified as being important for two reasons, because (1) it led to an increase in the yields of the monomers and oligomers; and (2) it inhibited the condensation reaction by suppressing the formation of the quinone methide intermediates. Conducting the pyrolysis in an aprotic solvent in the presence of a H-donor could therefore come to represent an effective method for the pyrolysis of lignin (Fig. 8). Dihydroconiferyl alcohol and isoeugenol would be formed as the major monomeric products under these conditions. The yields of the monomers [8.3 and 12.8 wt% from the MWL and the wood samples, respectively (DPE/H-donor/350°C)] were not small in comparison with the theoretical monomer yields described above.

Conclusions

329 Pyrolysis of coniferyl alcohol:

330 (1) Conducting the pyrolysis in DPB, which is an aprotic solvent, effectively inhibited
331 the polymerization of CA. This is probably through the inhibition of the proton-
332 transfer, which is as an important step required for the formation of the quinone
333 methide intermediates (a heterolysis reaction).

334 (2) The addition of the H-donor (1,2,3,10b-tetrahydrofluoranthene) led to an increase in
335 the yields of the side-chain reduction products (i.e., dihydroconiferyl alcohol and
336 isoeugenol) via the addition of a hydrogen radical (from the H-donor thermal
337 decomposition) to the C=C double bond of the side-chain in CA.

338

339 Pyrolysis of Japanese cedar (guaiacyl-type) lignin:

340 (1) The MWL and the wood samples gave coniferyl aldehyde, dihydroconiferyl alcohol,
341 isoeugenol and 4-vinylguaiacol as the monomeric guaiacols, together with CA. These
342 products were similar to those obtained from the pyrolysis of CA. These results
343 indicated that the CA pathway exists during the pyrolytic formation of the monomers
344 from lignin.

345 (2) Unlike for CA, both DPB and H-donor were required for effective formation of
346 monomer from MWL/wood. This can be explained by the stabilization of the CA
347 radical with the H-donor, as a primary product from the pyrolytic cleavage of the
348 ether linkages in lignin. Dihydroconiferyl alcohol and isoeugenol were the major
349 monomers under these conditions.

- (3) At the lower pyrolysis temperature of 250°C, coniferyl aldehyde was the major monomeric product from lignin, instead of CA. This can be explained with the H-donor/radical balance. More radical environment at such lower temperature would lead to oxidation of the C_γ in CA through abstraction of the C_γ-H by radical species.
- (4) The oligomeric products should also be focused as the initial products along with the monomers, because the condensed (C-C) linkages would be stable during the primary pyrolysis of lignin. The oligomeric products with relatively low volatilities preferentially condensed under the neat conditions. The use of DPB and H-donor significantly increased the yields of oligomers through stabilization against this condensation.
- (5) “Polymer effect” was suggested as a mechanism for promoting the secondary reactions of the lignin primary pyrolyzates.

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References

- [1] M. P. Pandey, C. S. Kim, Lignin depolymerization and conversion: A review of thermochemical methods, *Chem. Eng. Technol.* 34 (2011) 29-41.
- [2] D. Meier, J. Berns, C. Grünwald, O. Faix, Analytical pyrolysis and semicontinuous catalytic hydrolysis of organocell lignin, *J. Anal. Appl. Pyrolysis* 25 (1993) 335-347.
- [3] A. Oasmaa, A. Jphansson, Catalytic hydrotreating of lignin with water-soluble molybdenum catalyst, *Energy Fuels* 7 (1993) 426-429.
- [4] R. W. Thring, J. Breau, Hydrocracking of solvolysis lignin in a batch reactor, *Fuel* 75 (1996) 795-800.
- [5] M. Kleinert, T. Barth, Phenols from lignin, *Chem. Eng. Technol.* 31 (2008) 736-745.
- [6] H. Kawamoto, S. Horigoshi, S. Saka, Pyrolysis reactions of various lignin model dimers, *J. Wood. Sci.* 53 (2007) 168-174.
- [7] T. Nakamura, H. Kawamoto, S. Saka, Pyrolysis behavior of Japanese cedar wood lignin studied with various model dimers, *J. Anal. Appl. Pyrolysis* 81 (2008) 173-182.
- [8] R.J. Evans, T. A. Milne, Molecular characterization of the pyrolysis of biomass. 1. Fundamentals, *Energy Fuels*, 1 (1987) 123-137.

- [9] W. Genuit, J. J. Boon, O. Faix, Characterization of beech milled wood lignin by pyrolysis-gas chromatography-photoionization mass spectrometry, *Anal.Chem.* 59 (1987) 508-513.
- [10] J. Ralph, R. D. Hatfield, Pyrolysis-GC-MS characterization of forage materials, *J. Agric. Food Chem.* 39 (1991) 1426-1437.
- [11] K. Sipilä, E. Kuoppala, L. Fagernäs, A. Oasmaa, Characterization of biomass-based flash pyrolysis oils, *Biomass Bioenergy* 14 (1998) 103-113.
- [12] B. Scholze, D. Meier, Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). Part I. PY-GC-MS, FTIR, and functional groups, *J. Anal. Appl. Pyrolysis* 60 (2001) 41-54.
- [13] M.E. Arias, O. Polvillo, J. Rodríguez, M. Hernández, J.A. González-Pérez, F.J. González-Vila, Thermal transformations of pine wood components under pyrolysis/gas chromatography/mass spectrometry conditions, *J. Anal. Appl. Pyrolysis* 77 (2006) 63-67.
- [14] T. Kotake, H. Kawamoto, S. Saka, Pyrolysis reactions of coniferyl alcohol as a model of the primary structure formed during lignin pyrolysis, *J. Anal. Appl. Pyrolysis* 104 (2013) 573-584.
- [15] O. Faix, E. Jakab, F. Till, T. Székely, Study on low mass thermal-degradation products of milled wood lignins by thermogravimetry-mass-spectrometry, *Wood Sci. Technol.* 22 (1988) 323-334.

- [16] D.J. Gardner, T.P. Schultz, G.D. McGinnis, The pyrolytic behavior of selected lignin preparations, *J. Wood Chem. Technol.* 5 (1985) 85-110.
- [17] E. Jakab, O. Faix, F. Till, Thermal decomposition of milled wood lignins studied by thermogravimetry/mass spectrometry, *J. Anal. Appl. Pyrolysis* 40-41 (1997) 171-186.
- [18] T. Hosoya, H. Kawamoto, S. Saka, Pyrolysis behavior of wood and its constituent polymers at gasification temperature, *J. Anal. Appl. Pyrolysis* 78 (2007) 328-336.
- [19] N. Shimada, H. Kawamoto, S. Saka, Different action of alkali/alkaline earth metal chlorides on cellulose pyrolysis, *J. Anal. Appl. Pyrolysis* 81 (2008) 80-87.
- [20] C. P. Masuku, Thermolytic decomposition of coniferyl alcohol, *J. Anal. Appl. Pyrolysis* 23 (1992) 195-208.
- [21] T. Nakamura, H. Kawamoto, S. Saka, Condensation reactions of some lignin related compounds at relatively low pyrolysis temperature, *J. Wood Chem. Technol.* 27 (2007) 121-133.
- [22] H. Kawamoto, T. Nakamura, S. Saka, Pyrolytic cleavage mechanisms of lignin-ether linkages: A study on *p*-substituted dimers and trimers, *Holzforschung* 62 (2008) 50-56.
- [23] H. Kawamoto, M. Ryoritani, S. Saka, Different pyrolytic cleavage mechanisms of β -ether bond depending on the side-chain structure of lignin dimers, *J. Anal. Appl. Pyrolysis* 81 (2008) 88-94.

- [24] M. Asmadi, H. Kawamoto, S. Saka, The effect of combining guaiacol and syringol on their pyrolysis, *Holzforschung* 66 (2012) 323-330.
- [25] E. Adler, Lignin chemistry-past, present and future, *Wood Sci. Technol.* 11 (1977) 169-218.

Figure Legends

Fig. 1 HPLC chromatograms of the methanol-soluble portions obtained by the pyrolysis of coniferyl alcohol (CA), Japanese cedar MWL and wood, with identification of some signals (N_2 / 350°C/ 5min) .

IS (internal standard) : 1,2,3-trimethoxybenzene

Fig. 2 Influence of the addition of the aprotic solvent (diphenoxybenzene, DPB) and the H-donor (1,2,3,10b-tetrahydrofluoranthene) on the recovery of coniferyl alcohol and the yields of other monomeric guaiacols from the pyrolysis of coniferyl alcohol (CA) (CA 5.0mg/ N_2 /250-350°C/5min).

■ : coniferyl alcohol (<i>trans</i>) (1)	□ : coniferyl alcohol (<i>cis</i>) (2)
▨ : coniferyl aldehyde (3)	▤ : dihydroconiferyl alcohol (4)
▩ : isoeugenol (5)	□ : 4-vinylguaiacol (6)

Fig. 3 Influence of the addition of the aprotic solvent (diphenoxybenzene, DPB) and the H-donor (1,2,3,10b-tetrahydrofluoranthene) on the yields of monomeric guaiacols from the pyrolysis of Japanese cedar MWL and wood (MWL or wood 5.0mg/ N_2 /250-350°C/5min).

■ : coniferyl alcohol (<i>trans</i>) (1)	□ : coniferyl alcohol (<i>cis</i>) (2)
▨ : coniferyl aldehyde (3)	▤ : dihydroconiferyl alcohol (4)
▩ : isoeugenol (5)	□ : 4-vinylguaiacol (6)

Fig. 4 A proposed suppression mechanism of the aprotic solvent for the thermal polymerization of coniferyl alcohol (CA) (A) and a proposed role of the H-donor (1,2,3,10b-tetrahydrofluoranthene) as a source of the hydrogen radical for reduction of the side-chain double bond of CA (B).

Fig. 5 A proposed role of the H-donor and H-radical for the formation of the monomeric guaiacols during the pyrolysis of Japanese cedar lignin.

Fig. 6 Estimated yields of the monomeric and oligomeric units from a schematic softwood lignin structure comprising 16 C9 units [25], by assuming that all the ether linkages between aromatic ring and side-chain are cleaved without any further secondary decomposition.

Fig. 7 Influence of the addition of the aprotic solvent (1,3-diphenoxybenzene, DPB) and the H-donor (1,2,3,10b-tetrahydrofluoranthene) on the formation behaviors of the oligomeric products, as shown in the gel permeation chromatograms of the methanol-soluble portions obtained from the pyrolysis of Japanese cedar MWL or wood (MWL or wood 5.0 mg/ N_2 /250-350°C/5min).

a: retention time of coniferyl alcohol

— — — : 250°C - - - - : 300°C ——— : 350°C ——— : 350°C (+ H-donor)

*: H-donor : 1,2,3,10b-tetrahydrofluoranthene (11.4 mg/ 5.0 mg of MWL or wood)

Fig. 8 Conducting the pyrolysis in aprotic solvent in the presence of H-donor as an effective way to convert softwood lignin to dihydroconiferyl alcohol, isoeugenol and oligomers.

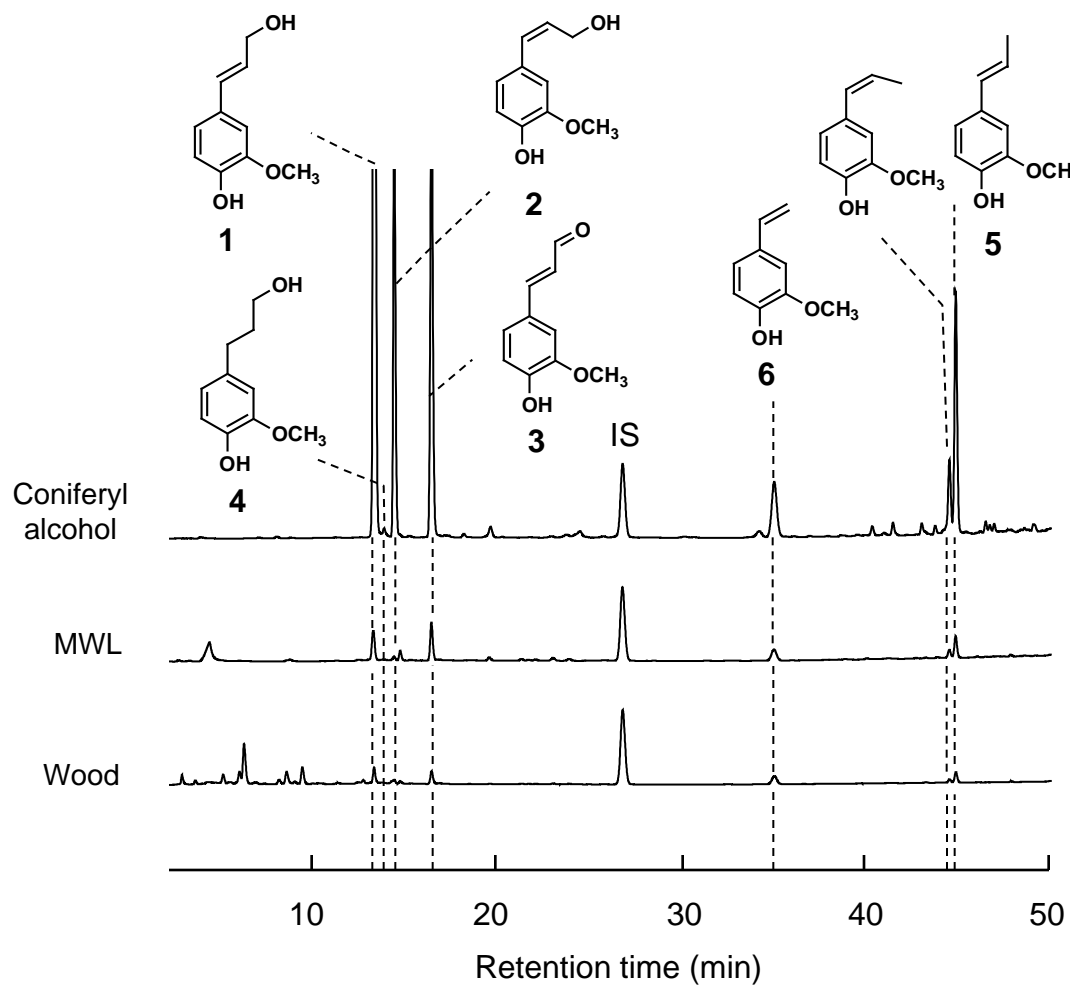


Fig. 1

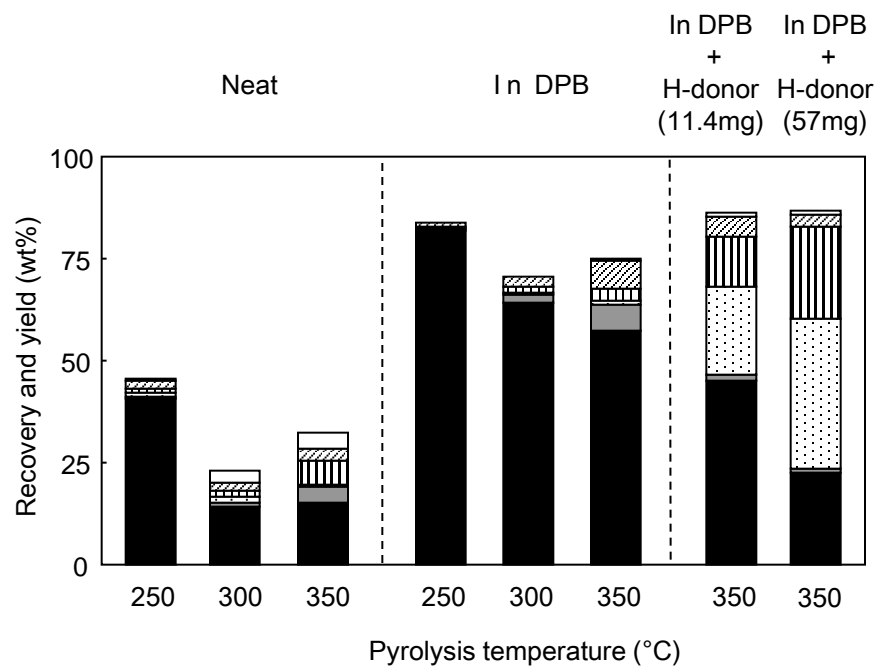


Fig. 2

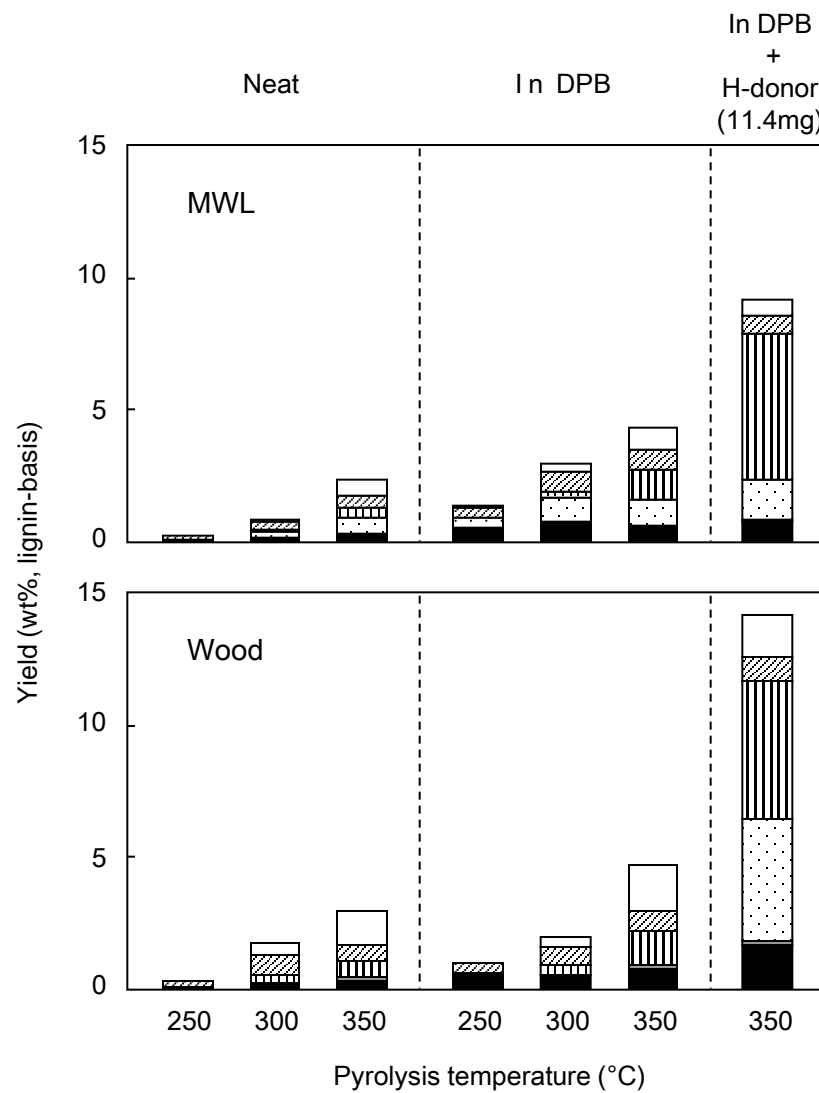
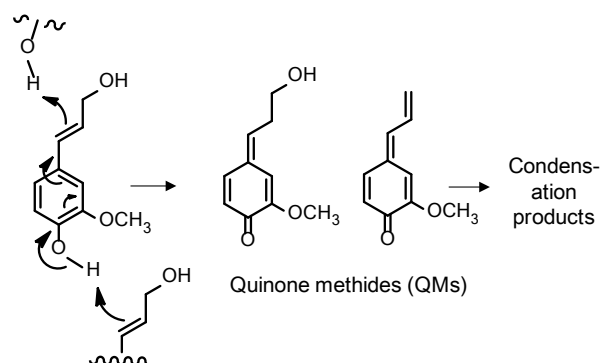


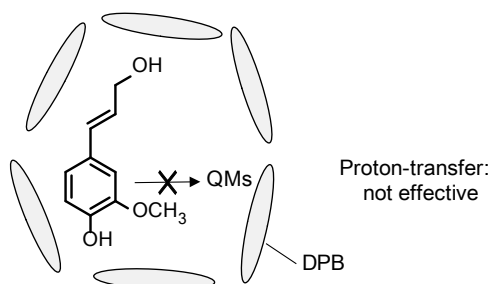
Fig. 3

A: Role of DPB

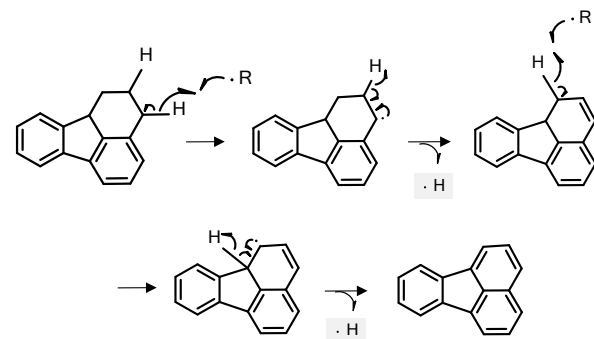
Neat condition



In DPB



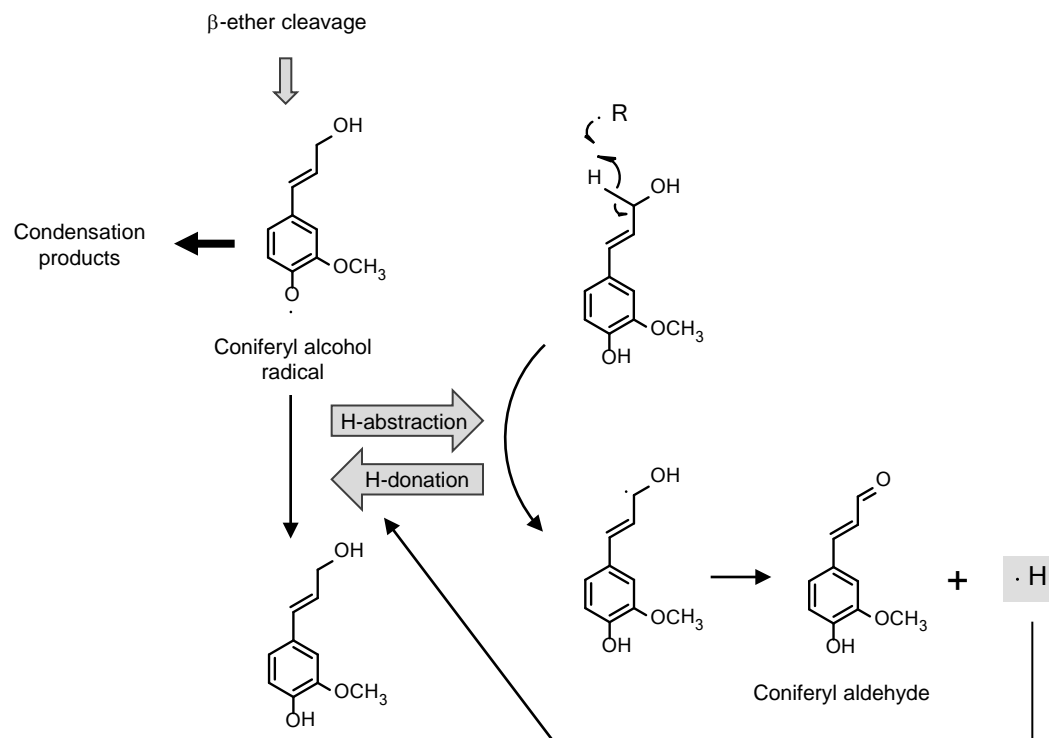
B: Role of H-donor



$\cdot H$ \Rightarrow Addition to $>C=C<$ \Rightarrow Dihydroconiferyl alcohol
Isoeugenol

Fig. 4

- Low temperature (such as 250°C) • H-deficient)



- High temperature (such as 350°C)

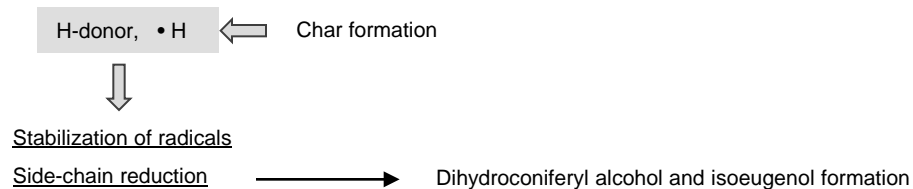
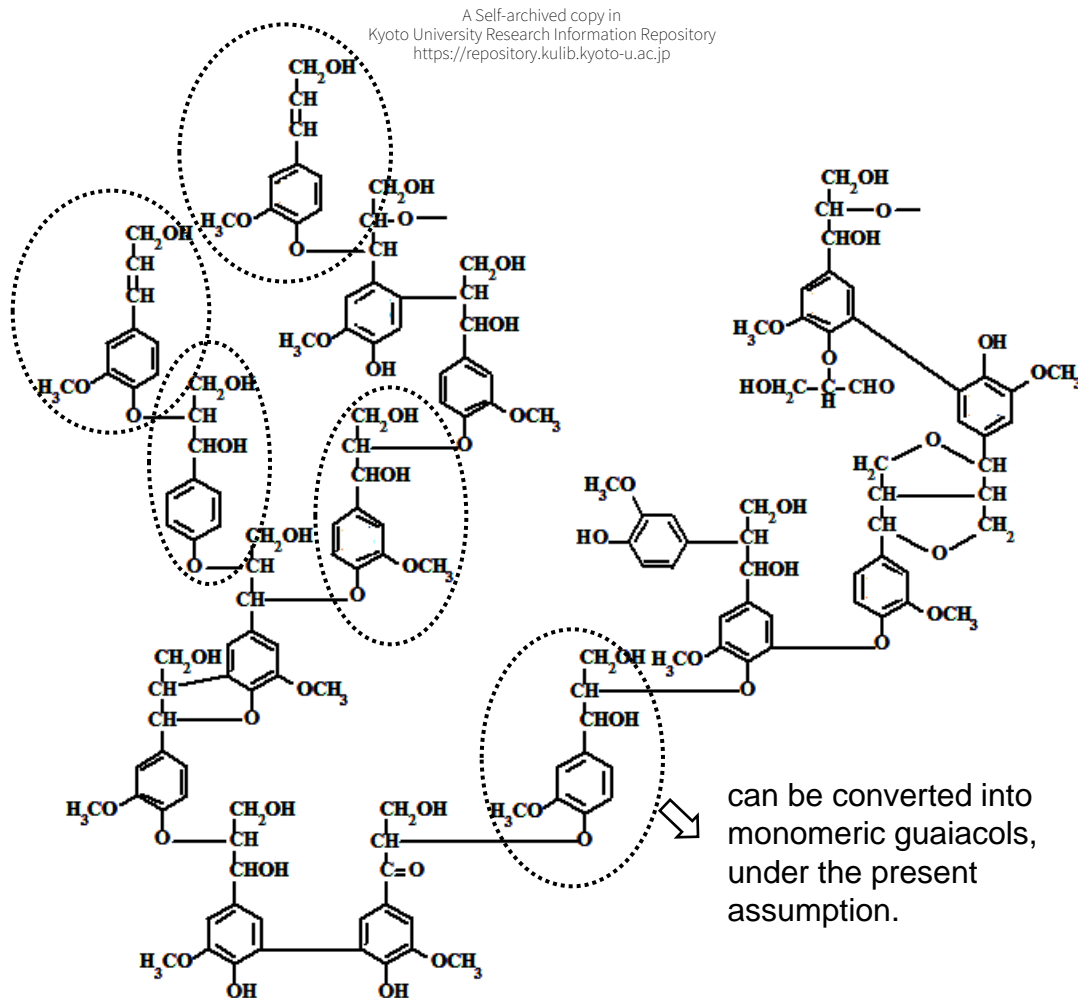


Fig. 5



can be converted into
monomeric guaiacols,
under the present
assumption.

$$\text{Estimated yield of monomeric guaiacols} = \frac{5}{16} \quad (31\%)$$

$$\text{Estimated yield of oligomers} = \frac{11}{16} \quad (69\%)$$

Fig. 6

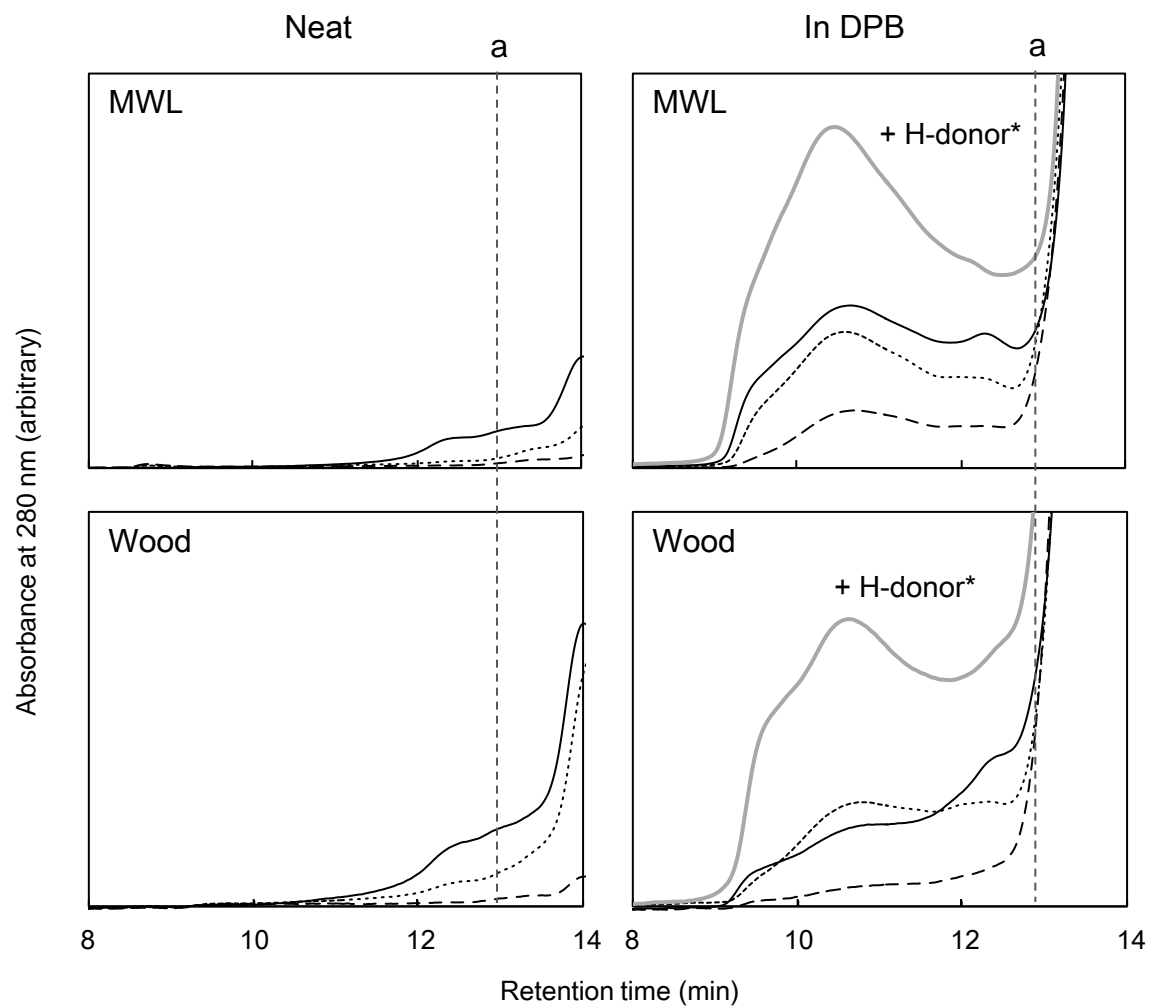


Fig. 7

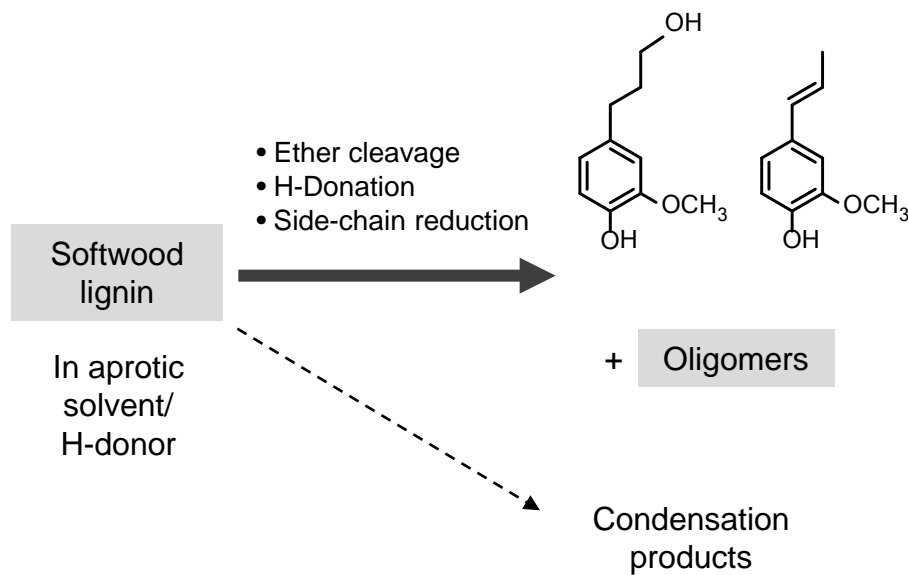


Fig. 8